Synthesis, characterization and photophysical properties of an acenaphthalene fused-ring-expanded NIR absorbing aza-BODIPY dye

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1.0 Experimental details for 1 and 2

Synthesis of 1,2-dibromoacenaphthylene (1)[1]

N-bromosuccinimide (21.36 g, 120 mmol) and a few crystals of dibenzoyl peroxide were added to a solution of acenaphthene (4.62 g, 30 mmol) in ethylacetate (150 mL), and the mixture was heated to reflux with stirring for 6 h. The deep orange mixture was cooled and the succinimide was removed by filtration. The solution was washed with aqueous sodium thiosulfate and the organic phase was dried over anhydrous magnesium sulphate. The solvent was evaporated under reduced pressure, and the brown liquid thus obtained was purified by column chromatography (silica gel, eluted with petroleum ether) to yield **1** as an orange solid. Yield: 7.2 g, 77%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.87 (d, 2H, J = 6 Hz), 7.69 (d, 2H, J = 6 Hz), 7.60 (t, 2H, J = 6 Hz), Anal. calcd for [$C_{12}H_6Br_2$]: C, 46.50; H, 1.95. Found: C, 46.32; H, 1.80.

Synthesis of 1,2-dicyanoacenaphthylene (2)[2]

Curpous cyanide (8.96 g, 100 mmol) was heated to 160°C in 70 mL of N-methyl-2-pyrrolidone with stirring under a nitrogen atmosphere, 1,2-dibromoacenaphthylene (7.58 g, 24.50 mmol) was then added. The reaction was continued at reflux with stirring under a nitrogen atmosphere for a further 4 h. The mixture was cooled and was quenched with a solution of sodium cyanide (12 g) in water (300 mL). The latter mixture was thoroughly shaken and then extracted with $CHCl_3$ (5 × 350 mL). The organic layer was further washed with 10% sodium cyanide solution (200 mL) and water (200 mL), subsequently dried over anhydrous sodium sulfate, and evaporated under reduced pressure. The brown liquid thus obtained was purified by column chromatography (silica gel, eluted with 2:1 $CHCl_3$-petroleum ether (v/v) to yield **2** as a yellow solid. Yield: 3.2 g, 65%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.25 (d, 2H, J = 12 Hz), 8.20 (d, 2H, J = 6 Hz), 7.86 (t, 2H, J = 12 Hz), Anal. calcd for [$C_{14}H_6N_2$]: C, 83.16; H, 2.99; N, 13.85. Found: C, 82.96; H, 2.82; N, 13.68.

2.0 NMR of 1-4

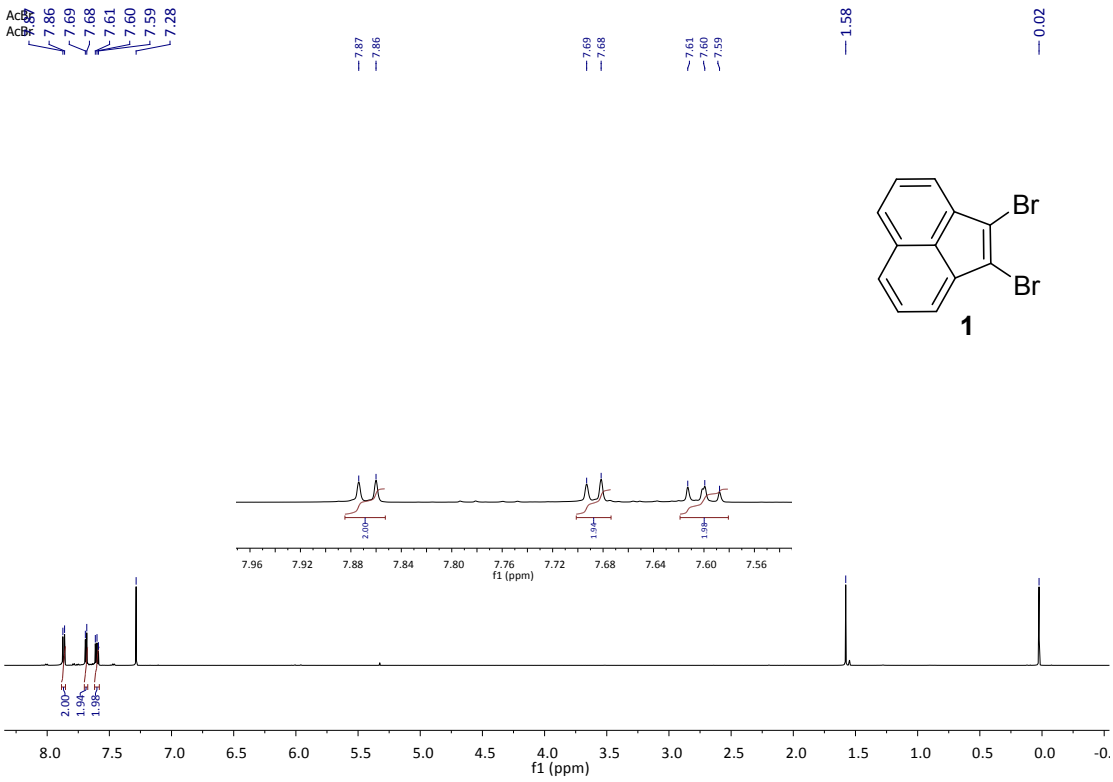

Fig S1 ^{1}H NMR spectrum of 1,2-dibromoacenaphthylene **1** (600 MHz, $CDCl_3$)

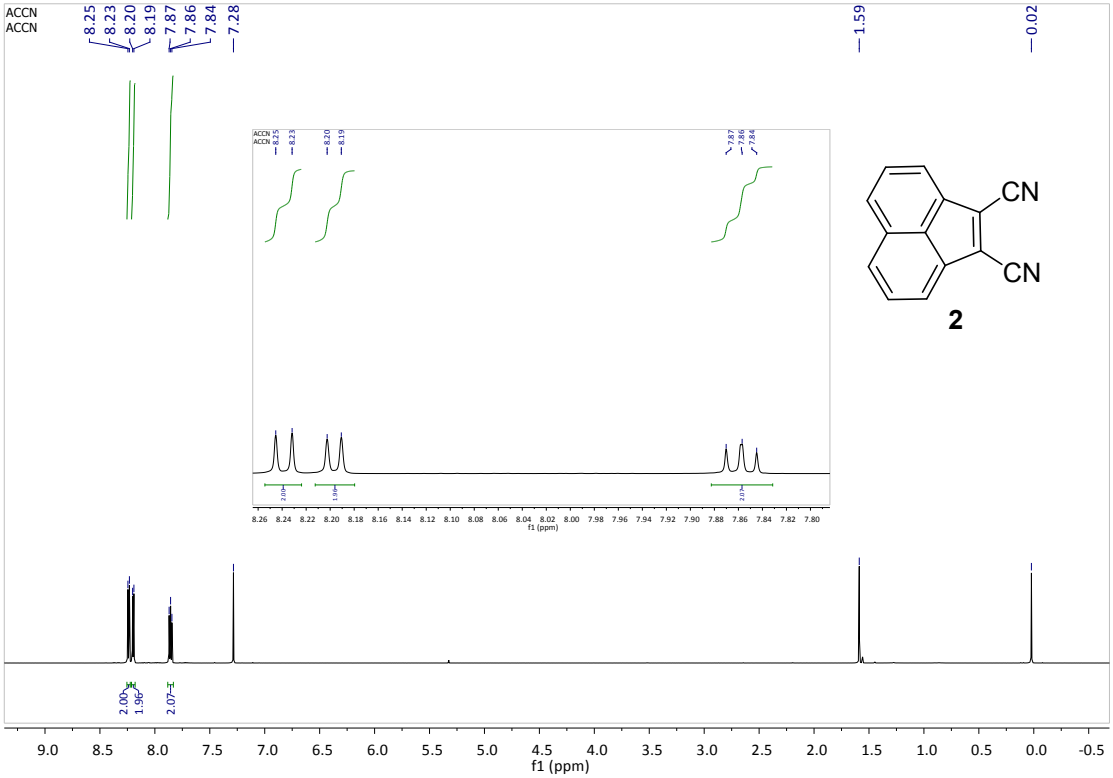

Fig S2 ^{1}H NMR spectrum of 1,2-Dicyanoacenaphthylene **2** (600 MHz, $CDCl_3$)

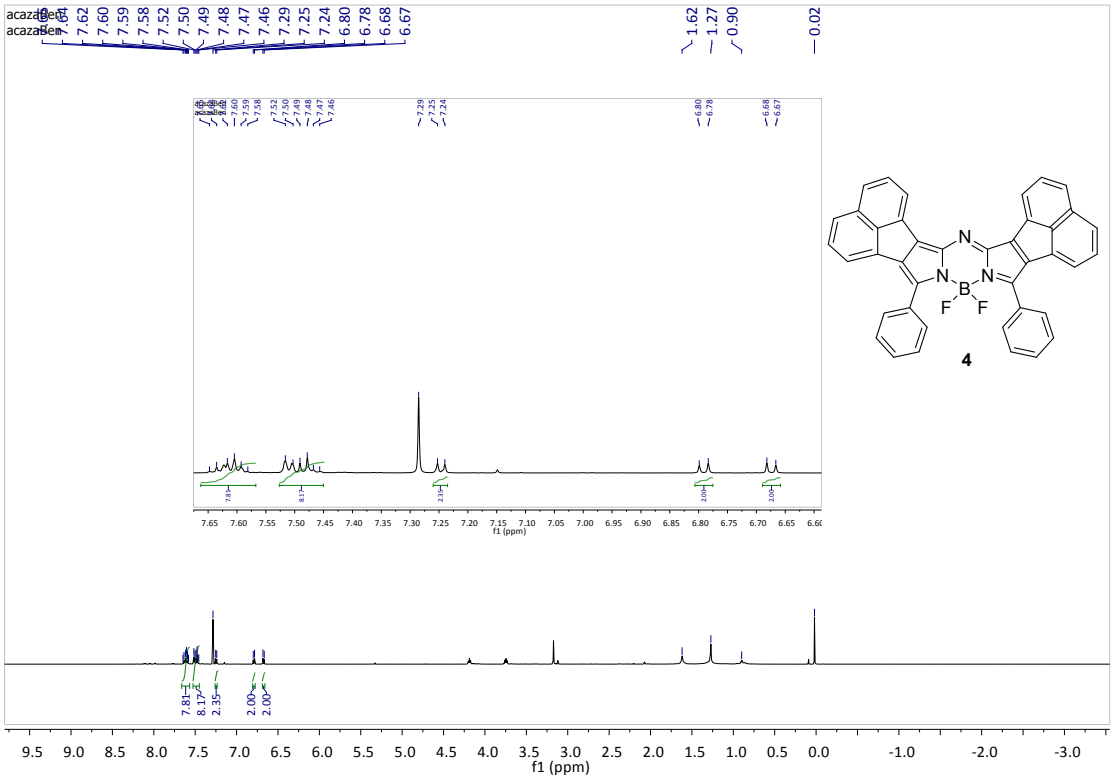

Fig S3 ^{1}H NMR spectrum of aza BODIPY **4** (600 MHz, $CDCl_3$)

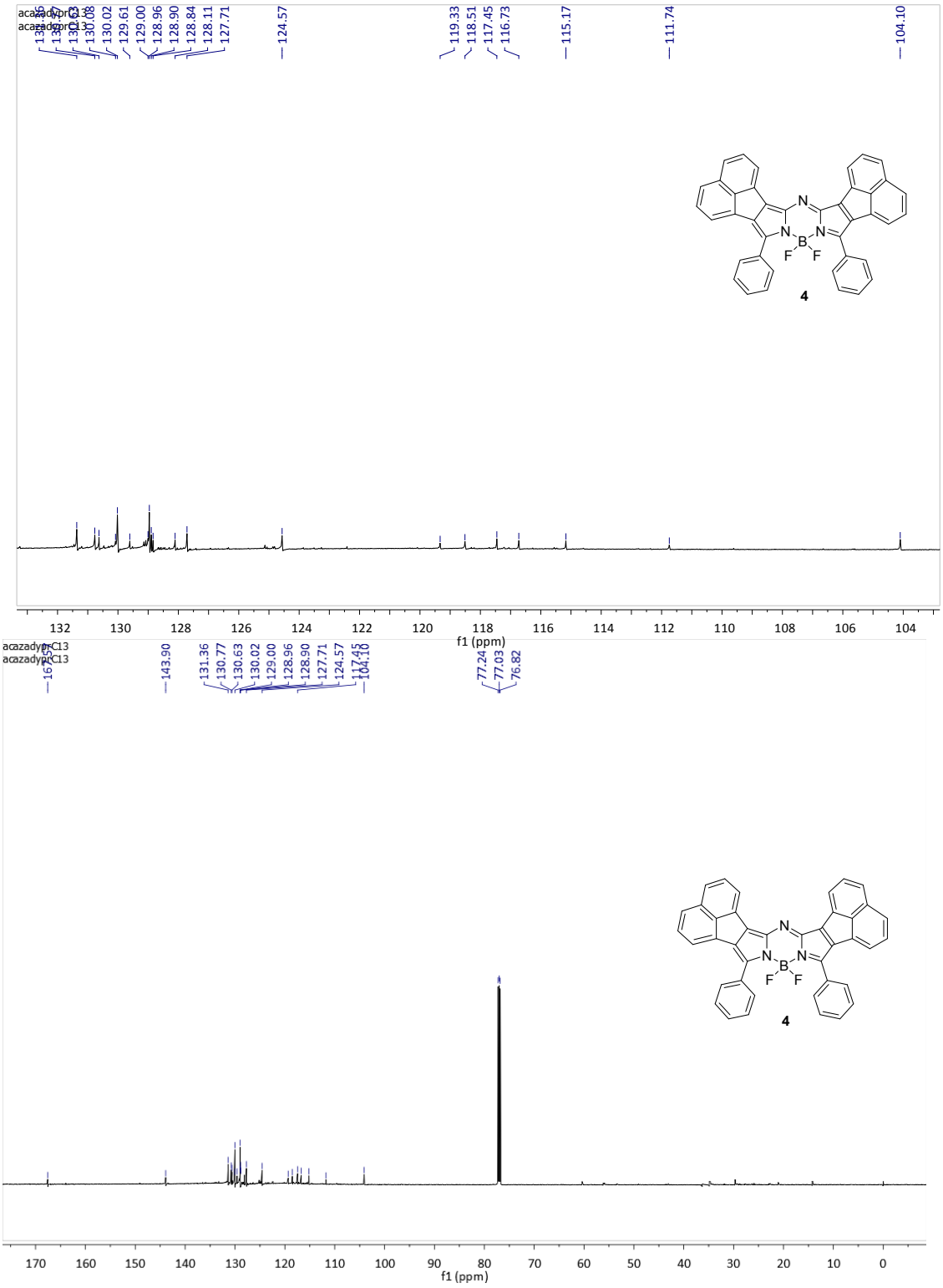

Fig S4 ^{13}C NMR spectrum of aza BODIPY **4** (150 MHz, $CDCl_3$)

3.0 References

1. B. M. Trost and D. R. Britelli*, J. Org. Chem.*, 1967, **32**, 2620.

2. D. A. Herold and R. D. Rieke, *J. Org. Chem.*, 1979, **44**, 1359.